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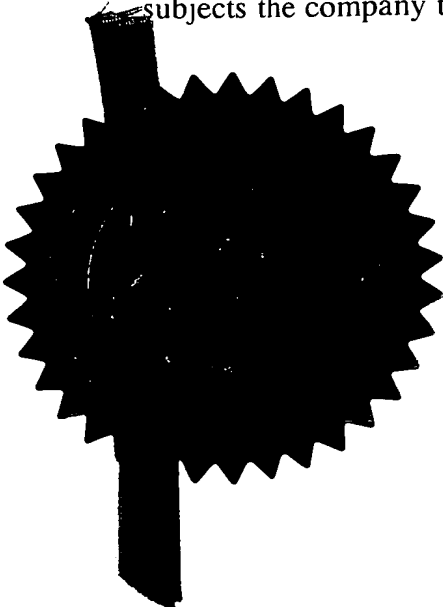
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Request for grant of a patent

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21 AUG 1999

The Patent Office

Cardiff Road
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1. Your reference

15431 MdCm

2. Patent application number

(The Patent Office will fill in this part)

9919807.9

3. Full name, address and postcode of the or of each applicant (underline all surnames)

AEA Technology plc
329 Harwell
Didcot, Oxfordshire, OX11 0RA
United Kingdom

Patents ADP number (if you know it)

If the applicant is a corporate body, give the country/state of its incorporation

England and Wales 6969372001

4. Title of the invention

Anode for rechargeable lithium cell

5. Name of your agent (if you have one)

"Address for service" in the United Kingdom to which all correspondence should be sent (including the postcode)

Peter Turquand Mansfield
AEA Technology plc
Patents Department, 329 Harwell
Didcot, Oxfordshire, OX11 0RA

Patents ADP number (if you know it)

6969372002

6. If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and (if you know it) the or each application number

Country

Priority application number
(if you know it)

Date of filing
(day / month / year)

7. If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application

Number of earlier application

Date of filing
(day / month / year)

8. Is a statement of inventorship and of right to grant of a patent required in support of this request? (Answer 'Yes' if:

- a) any applicant named in part 3 is not an inventor, or
 - b) there is an inventor who is not named as an applicant, or
 - c) any named applicant is a corporate body.
- See note (d))

Yes

Patents Form 1/77

9. Enter the number of sheets for any of the following items you are filing with this form.
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Continuation sheets of this form

Description

6

Claim(s)

-

Abstract

1

Drawing(s)

-

10. If you are also filing any of the following, state how many against each item.

Priority documents

Translations of priority documents

Statement of inventorship and right to grant of a patent (Patents Form 7/77)

Request for preliminary examination and search (Patents Form 9/77)

Request for substantive examination (Patents Form 10/77)

Any other documents (please specify)

11.

I/We request the grant of a patent on the basis of this application.

Signature

Date

20.08.99

M.J. LOFTING (On behalf of AEA Technology plc
by virtue of a Power of Attorney dated 26th March 1996)

12. Name and daytime telephone number of person to contact in the United Kingdom

01235 432037 Mrs C A Cassidy

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Notes

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Anode for Rechargeable Lithium Cell

This invention relates to an anode for a rechargeable lithium cell, and to a cell incorporating
5 such an anode.

For many years it has been known to make cells with lithium metal anodes, and cathodes of a material into which lithium ions can be intercalated or inserted. A
10 wide variety of intercalation or insertion materials are known as cathode materials for rechargeable lithium cells, such as TiS_2 , V_6O_{13} and Li_xCoO_2 where x is less than 1; and these materials are often mixed with solid electrolyte material to form a composite cathode. To
15 avoid the problems arising from dendrite growth at lithium metal anodes during cycling, it has been proposed to use an intercalation material such as graphite as the anode material, and this also may be mixed with solid electrolyte material to form a composite anode.
20 Rechargeable cells of this type, in which both the anode and cathode contain intercalated lithium ions, are now available commercially, and may be referred to as lithium ion cells, or as swing or rocking-chair cells.

25 Another known possibility is to use, as the anode material, a metal such as aluminium that forms an alloy with lithium. However, repeated cycling of a cell with a lithium/aluminium alloy anode leads to volumetric changes and structural damage. Tin oxide has also been suggested
30 as a reversible anode material in a lithium ion cell. The lithium insertion process is believed to proceed by the initial reduction of the tin oxide, followed by reversible formation of the lithium alloy. While the

repeated insertion and removal of lithium into bulk tin metal tends to show poor reversibility due to large volumetric changes, improved stability of tin oxide anodes is observed due to the presence of an oxide
5 framework surrounding the metallic tin particles.

According to the present invention an anode for a rechargeable lithium cell comprises carbon nanotubes that
10 contain within them a metal or a metalloid that can form alloys reversibly with lithium over a range of compositions.

Preferably the metal or metalloid within the
15 nanotubes is a metallic element such as aluminium or tin, or a metallic alloy such as antimony/tin, but it may also be possible for it to be a metalloid such as silicon. The term alloy should be understood as encompassing both conventional alloys and lithium/elemental compounds of
20 the general formula MLi_x , where M represents the other element (metal or metalloid) and x may have a range of different values.

Preferably the carbon nanotubes are bound together
25 by a polymeric binder, which may for example be polyvinylidene fluoride.

The present invention also provides a rechargeable lithium cell incorporating an anode as specified above, a
30 reversible cathode, and an electrolyte. The electrolyte may be either a solid polymeric electrolyte, or a liquid electrolyte. Where the electrolyte is a liquid, an inert, liquid-permeable separator is usually provided to

separate the anode from the cathode. A variety of different intercalation materials may be used in such a cathode.

5 Such a cell can be expected to have improved capacity and improved reversibility, because the nanotubes will provide a stabilising framework for the alloy. The carbon nanotubes may also provide additional lithium intercalation capacity.

10

Carbon nanotubes are tube-like structures of diameter no more than a few nanometres, but which may be several microns in length. They can be considered as a sheet or hexagonal lattice of carbon atoms (as in a layer
15 of graphite) which has been rolled up to make a cylinder, with a hemispherical cap like half a fullerene molecule at each end. The nanotubes can be characterized by their diameter, and their helicity, which is determined by the axis about which the sheet is rolled. They have been made
20 by laser vaporisation of a carbon target in a furnace, in the presence of a cobalt/nickel catalyst; they have also been made using a carbon arc.

~~The~~ The invention will now be further and more
25 particularly described, by way of example only. Carbon nanotubes are prepared electrolytically, by using a carbon electrode as cathode in a bath of molten salt, such as sodium chloride. It is believed that, on the application of current, sodium is forced into the
30 graphite structure and this induces the extrusion of the nanotubes. A less stable salt, such as tin chloride, is also introduced into the molten salt bath. This decomposes first, and the resulting metal (tin) is

initially deposited onto the surface of the graphite. It is found that the nanotubes resulting from this procedure contain the metal of the less stable salt inside the nanotubes. After electrolysis, the salt is dissolved in
5 water; the nanotubes remain in suspension, but will collect at the interface between the aqueous solution and an immiscible organic liquid. In this way the nanotubes can be produced with high yield.

10 The tin-filled nanotubes made as described above are thoroughly dried. The nanotubes are then used to make an anode, by mixing 90 parts by weight of the nanotubes with 10 parts of polyvinylidene fluoride homopolymer (PVdF), forming a slurry with N-methyl pyrrolidone (NMP) as
15 solvent for the PVdF, casting onto a copper foil current collector, and thoroughly drying the cast layer to remove the NMP solvent. A similar procedure is then used to make a cathode, mixing lithium cobalt oxide, carbon and PVdF with NMP as solvent to form a slurry, casting onto
20 an aluminium foil current collector, and thoroughly drying the cast layer to remove the NMP solvent. The anode and the cathode are then separated by a microporous polyethylene separator, wound up to form a coil, and inserted into a can. The can is then filled with organic
25 liquid electrolyte consisting of 1M LiPF_6 dissolved in ethylene carbonate/ethyl methyl carbonate mixture, and sealed.

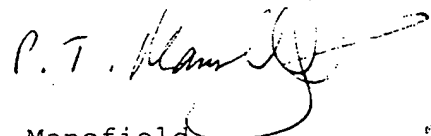
It will be appreciated that an anode comprising only
30 nanotubes and a polymer binder (such as polyvinylidene fluoride) is suitable where the anode is to be used in a cell with a liquid electrolyte. An alternative anode incorporates plasticising solvent (such as ethylene

carbonate or propylene carbonate) along with the nanotubes and the polymer binder, and a lithium salt, and is suitable for use with a solid polymer electrolyte. A further alternative anode incorporates plasticising solvent, nanotubes and polymer binder, but no lithium salt. Such an anode would be easier to handle, as an anode containing lithium salt must be kept in a totally dry environment.

10 To produce aluminium-filled nanotubes the electrolysis process is substantially the same as that described earlier, except that the less stable salt to be added to the molten salt bath is aluminium chloride.

15 Thus an alternative cell may be made as follows, using aluminium-filled nanotubes that have been thoroughly dried. Forty eight parts of the nanotubes are mixed with 24 parts of the volatile solvent tetrahydrofuran to produce a slurry (all parts are parts by weight). This is then mixed with a polymer solution containing six parts of a PVdF copolymer, 30 parts of salt solution (1 M LiPF_6 in a mixture of three parts ethylene carbonate to two parts propylene carbonate), and 40 parts tetrahydrofuran. This mixture is then cast, using a doctor blade over a roller with a blade gap 0.5 mm, onto a copper foil, and passed through a dryer at 70°C to ensure evaporation of the volatile solvent tetrahydrofuran. In this particular example the copolymer is of vinylidene fluoride with 2 percent by weight of hexafluoropropylene, and has a sufficiently high molecular weight that its melt flow index (at a temperature of 230°C and a load of 21.6 kg) is only 3.1 g/10 min.

The resulting anode comprises the aluminium-filled nanotubes along with copolymer, plasticising solvents and lithium salt. It can be combined with a composite
5 cathode and a polymer electrolyte to form a reversible lithium ion cell.



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10

P.T. Mansfield
Chartered Patent Agent
Agent for the Applicants

Abstract

Anode for Rechargeable Lithium Cell

5 An anode for a rechargeable lithium cell comprises
carbon nanotubes that contain within them an element that
can form alloys or compounds reversibly with lithium over
a range of compositions. The element within the
nanotubes may be aluminium or tin. These carbon
10 nanotubes are bound together to form a coherent layer
with a polymeric binder, such as a polymer of vinylidene
fluoride. A cell with such an anode should have improved
capacity and improved reversibility, because the
nanotubes provide a stabilising framework for the alloy.

15

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